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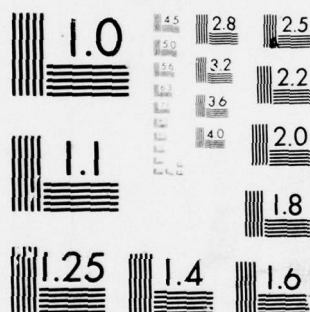
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POLYMERIZATION OF SPIRO ORTHO ESTERS — EFFECT OF TEMPERATURE ON KINETIC RESULTS

BY HUBERT J. BOOTH

RESEARCH AND TECHNOLOGY DEPARTMENT

AUGUST 1978

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SUMMARY

This report describes kinetic data obtained on the polymerization of spiro ortho esters as a function of temperature. Spiro ortho esters represent a class of monomers that have near zero shrinkage or slight expansion when polymerized. The results obtained indicated that temperatures down to -30°C do not prevent interfering side reactions from occurring.

This work was performed with funding from Internal Research, Task No. CR01AA171. The work was conducted during the period October 1977 through May 1978.

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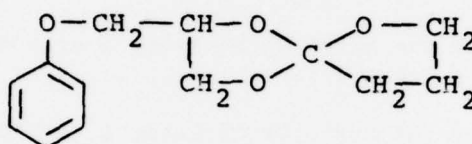
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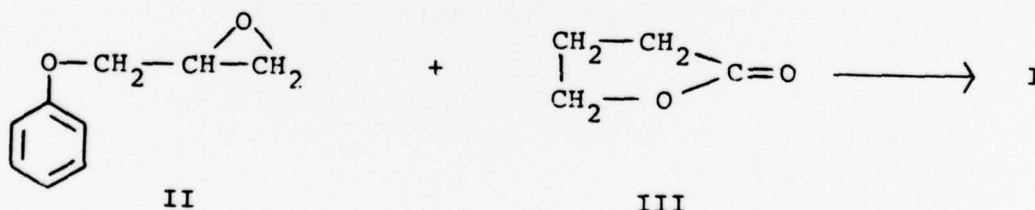
INTRODUCTION

The potential usefulness of monomers that expand--rather than shrink--upon polymerization has been detailed in our first report.¹ In that report we explained the reasons why the spiro ortho ester I, 2-phenoxyethyl-1,4,6-trioxaspiro(4.4)nonane, was chosen as the model compound for kinetic study.



I

The results given in that report showed that this monomer underwent various side reactions during its polymerization. The side reactions affect the final polymer in such a way that its composition and structure are unknown. Basically, the side reactions result from the breakdown of I, upon addition of the boron trifluoride etherate catalyst, to the compounds from which it is prepared, phenyl glycidyl ether, II, and γ -butyrolactone, III. Consequently, II can undergo several reactions (detailed in Reference 1) that affect the makeup of the final polymer.



Therefore, in an effort to control or prevent these side reactions, kinetic studies were performed at temperatures below room temperature. (Room temperature was the temperature at which polymerization data was gathered and given in Reference 1.)

1. Booth, Hubert J., Polymerization of Spiro Ortho Esters - Preliminary Kinetic Results, NSWC/WOL TR 77-103, 24 August 1977.

EXPERIMENTAL

The materials used and the gas chromatographic equipment and the calibration of that equipment are explained in Reference 1. Methylene chloride was used exclusively as the polymerization solvent; boron trifluoride etherate was used as the polymerization catalyst. Kinetic studies could not be conducted below -30°C because the spiro ortho ester I crystallized from solution below -30°C . The starting concentration of the spiro ortho ester I in methylene chloride was held constant in all the kinetic runs.

RESULTS AND DISCUSSION

I. Polymerization at 15°C

A. Five Mole Percent Catalyst

The data gathered on the polymerization of I in methylene chloride at 15°C using 5 mole percent boron trifluoride etherate is given in Figure 1. The results show that upon addition of catalyst a portion of the spiro ortho ester I quickly dissociates to phenyl glycidyl ether, II, and γ -butyrolactone, III. The concentrations of II and III would be equal if II did not undergo the various side reactions explained in Reference 1.

B. Ten Mole Percent Catalyst

Figure 2 shows the results of the kinetic run at 15°C with 10 mole percent catalyst. As expected based on the data obtained in the preliminary kinetic results (Reference 1), the catalyst concentration directly affects the quasi-equilibrium concentrations of I, II, and III.

II. Polymerization at 0°C

A. Five Mole Percent Catalyst

The results of the kinetic run at 0°C and 5 mole percent catalyst are given in Figure 3. The data is essentially the same as that obtained at 15°C and 5 mole percent catalyst (Figure 1). A decrease of 15°C (from 15°C to 0°C), therefore, had little or no effect on the polymerization rate or side reactions.

B. Ten Mole Percent Catalyst

Once again the data given in Figure 4 for 0°C and 10 mole percent catalyst is, within experimental error, the same as that data obtained at 15°C and 10 mole percent catalyst (Figure 2).

III. Polymerization at -20°C

A. Ten Mole Percent Catalyst

Figure 5 gives the results gathered at -20°C and 10 mole percent catalyst. The data corresponds well with that obtained with 10 mole percent catalyst at 15°C and 0°C (Figures 2 and 4).

B. Two Separate Additions of Five Mole Percent Catalyst for Total of Ten Mole Percent Catalyst

In this case, we wanted to determine if the effect of catalyst on the quasi-equilibrium concentrations of compounds I, II, and III was cumulative. The results in Figure 6 show that the effect of catalyst is cumulative. The data obtained after the first addition of 5 mole percent catalyst is the same as the data gathered at 15°C and 0°C (Figures 1 and 3). After 243 minutes, the second addition of 5 mole percent catalyst was added and gave results comparable to the data given for 15°C, 0°C, and -20°C at 10 mole percent catalyst (Figures 2, 4, and 5).

IV. Polymerization at -30°C

A. Five Mole Percent Catalyst

Again the data given for these conditions (Figure 7) is the same as the results obtained for the other temperatures at 5 mole percent catalyst (Figures 1 and 3).

B. Ten Mole Percent Catalyst

Figure 8 shows the results gathered at -30°C and 10 mole percent catalyst. The data compares favorably with that obtained at the other temperatures using 10 mole percent catalyst (Figures 2, 4, and 5).

C. Twenty Mole Percent Catalyst

The results of adding 20 mole percent catalyst to the polymerization solution at -30°C are given in Figure 9. As expected, different amounts of catalyst directly affect the quasi-equilibrium concentrations of compounds I, II, and III.

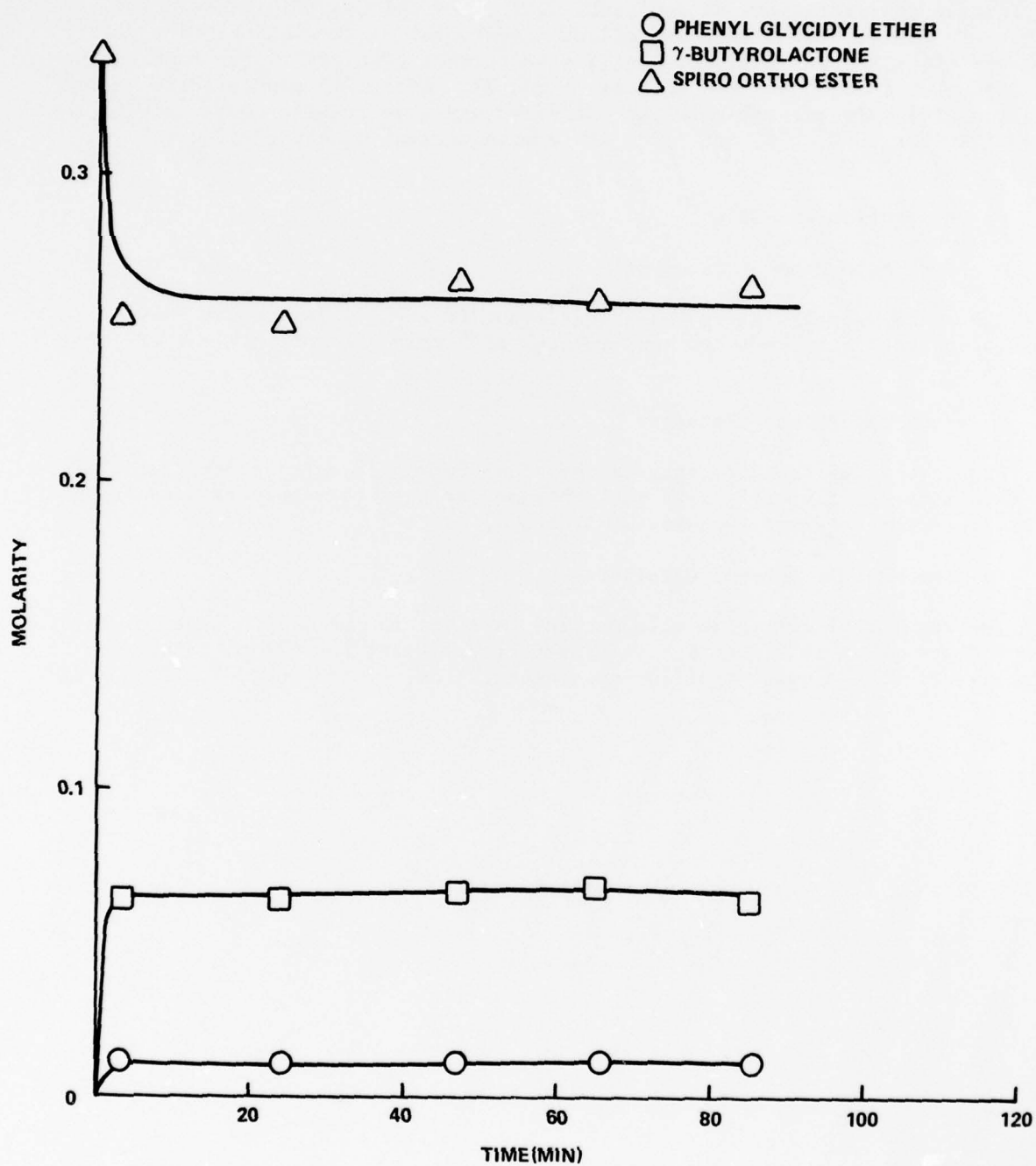


FIGURE 1 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT 15°C AND FIVE MOLE PERCENT CATALYST

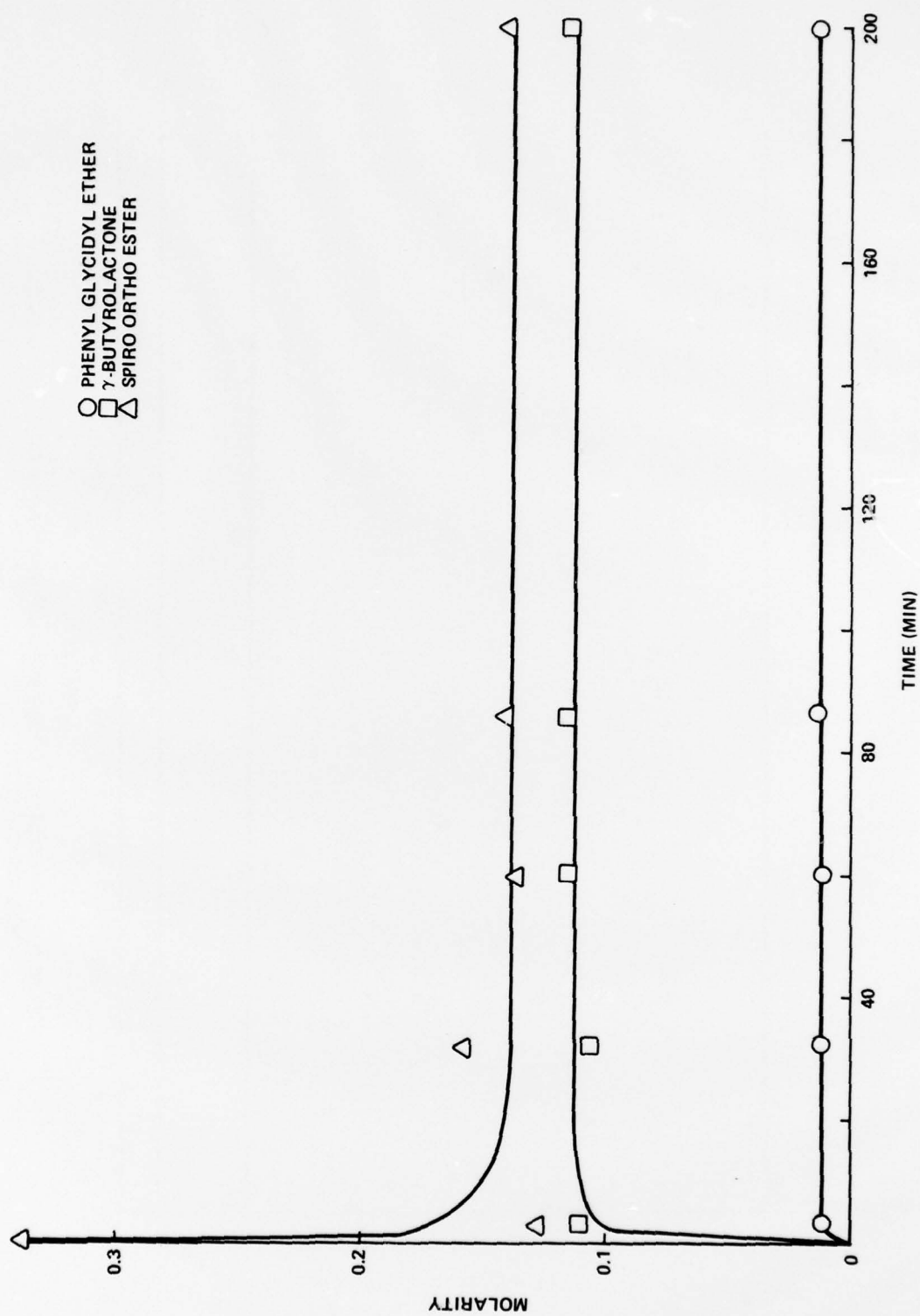


FIGURE 2 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT 15°C AND TEN MOLE PERCENT CATALYST

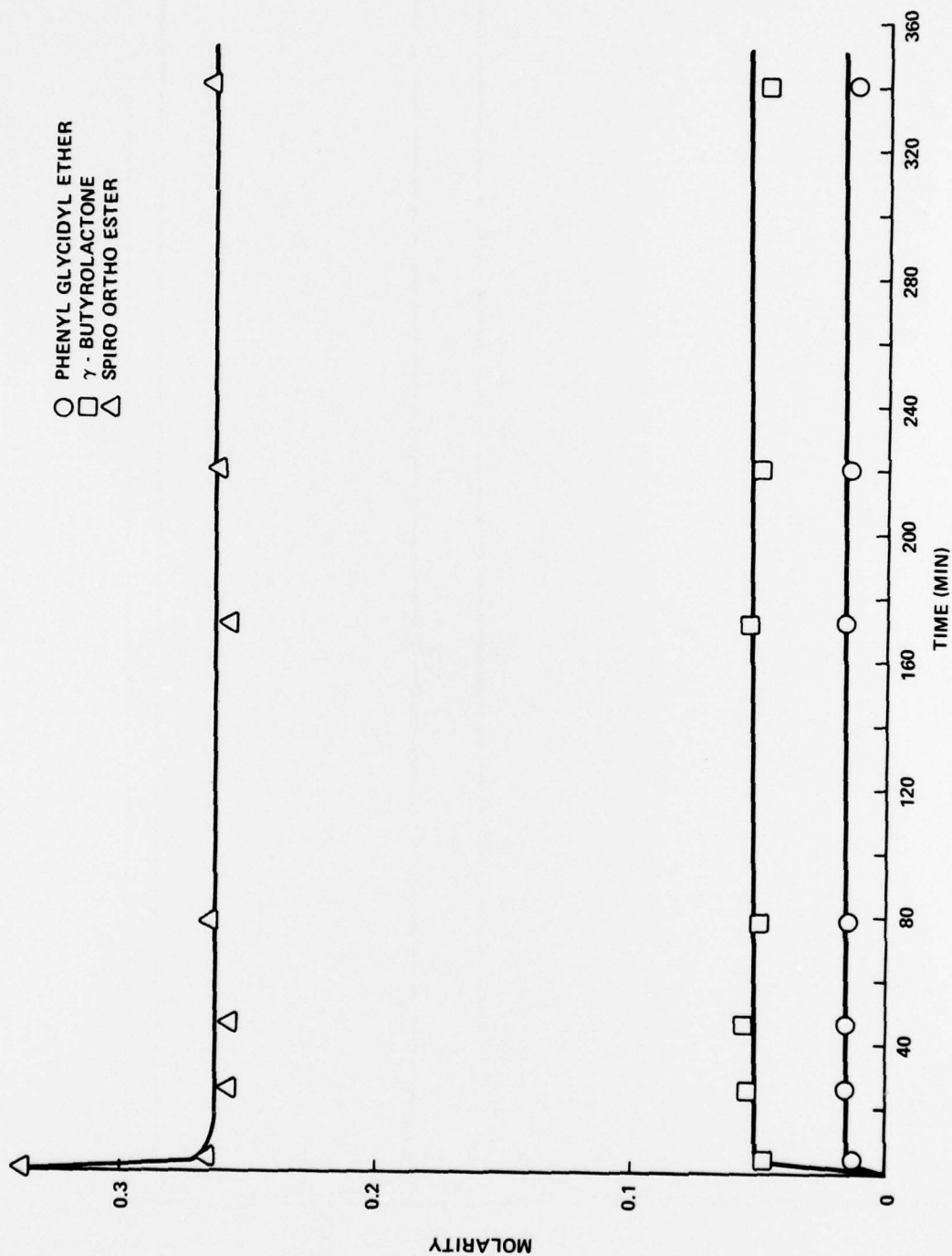


FIGURE 3 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT 0°C AND FIVE MOLE PERCENT CATALYST

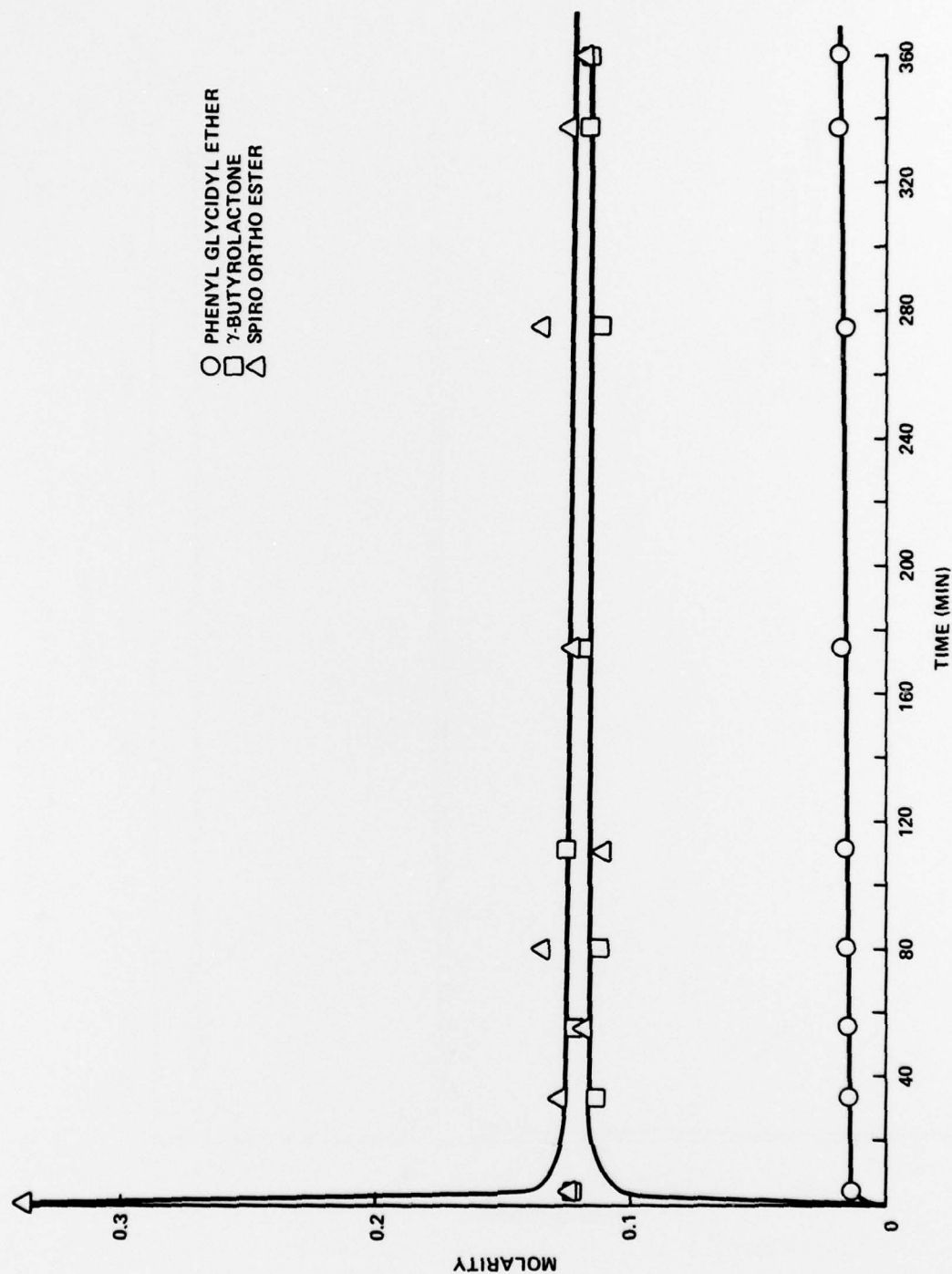
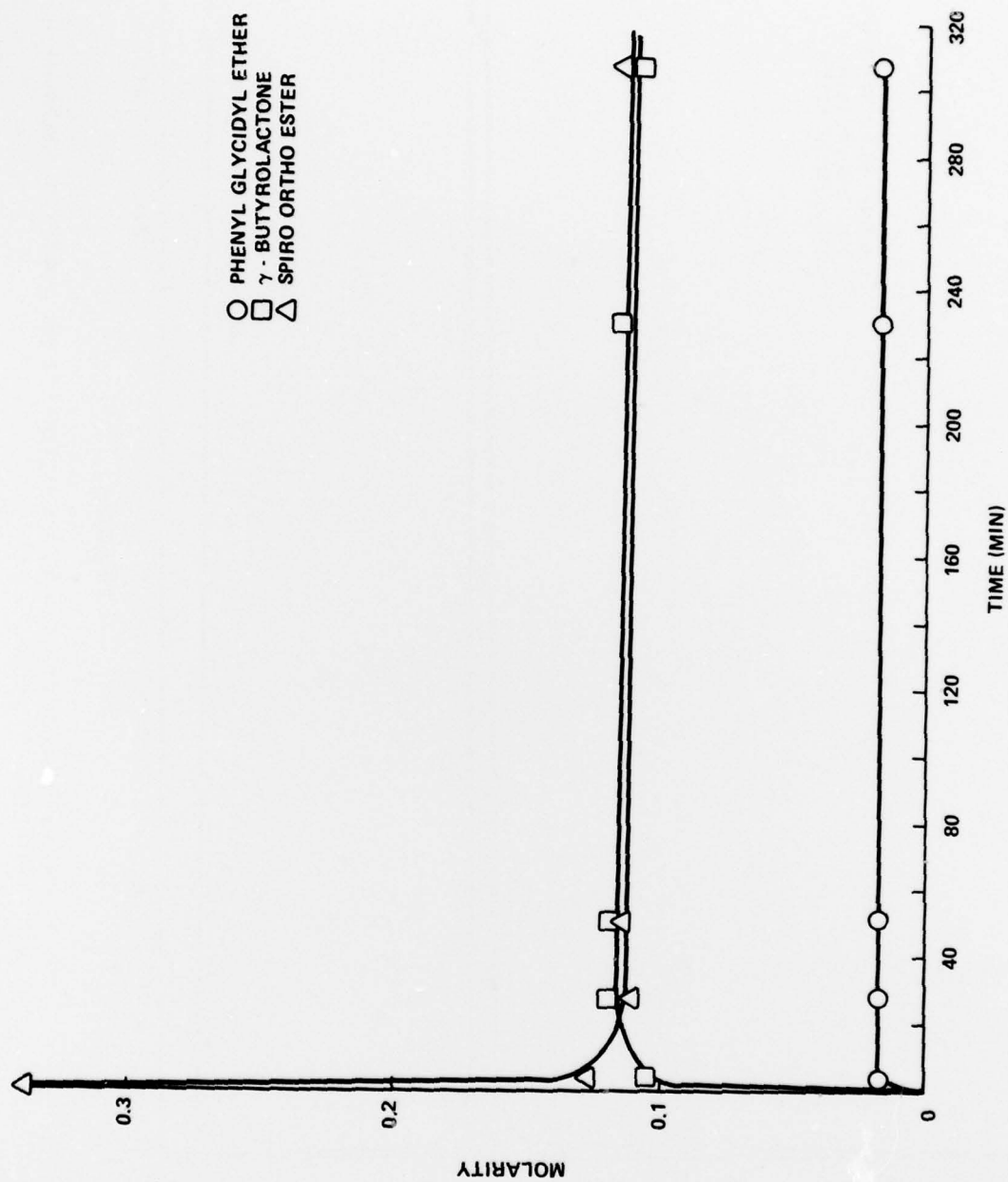


FIGURE 4 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT 0°C AND TEN MOLE PERCENT CATALYST

FIGURE 5 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT -20°C AND TEN MOLE PERCENT CATALYST

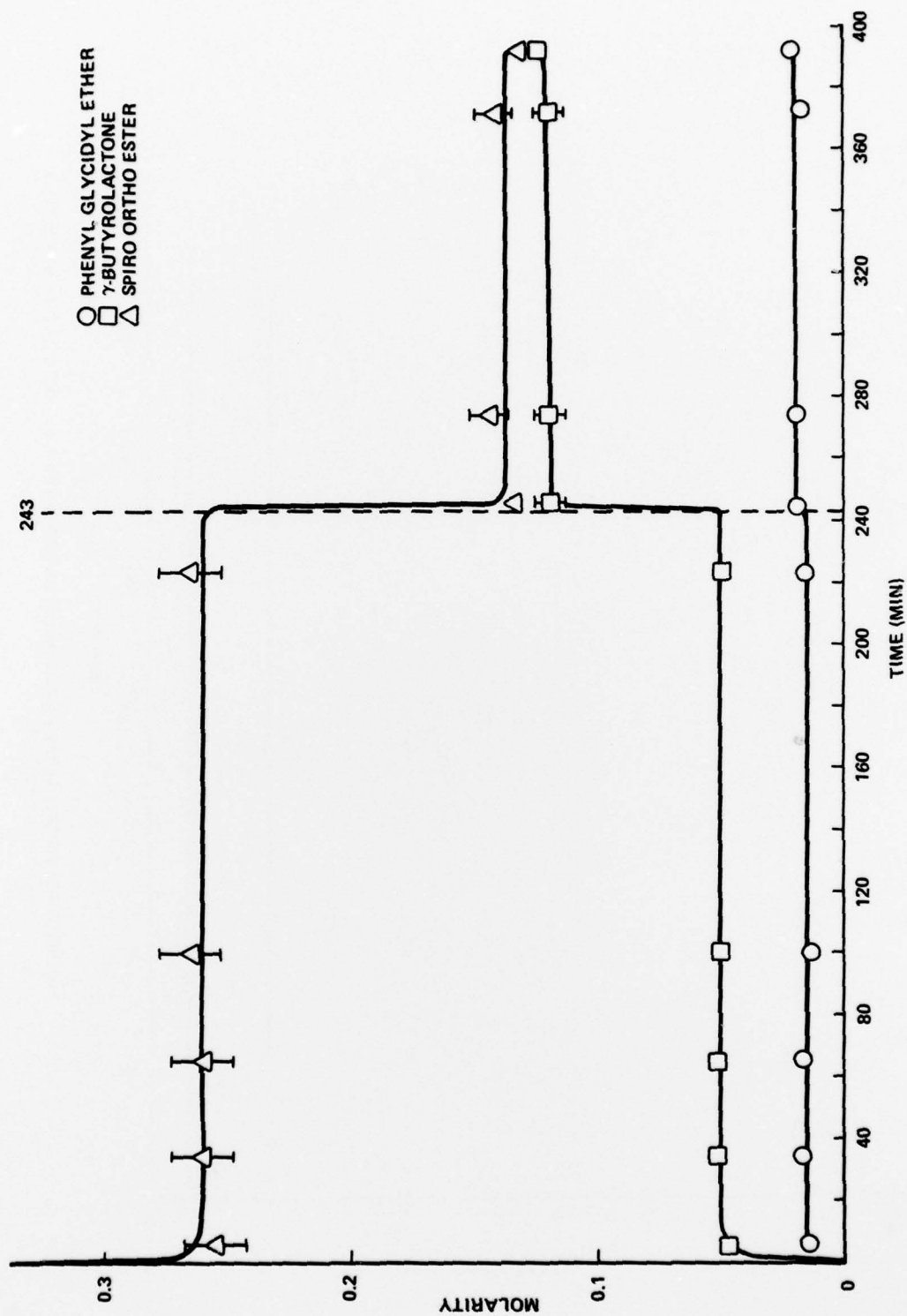


FIGURE 6 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT -20°C AND TWO SEPARATE ADDITIONS OF FIVE MOLE PERCENT CATALYST FOR A TOTAL OF TEN MOLE PERCENT CATALYST

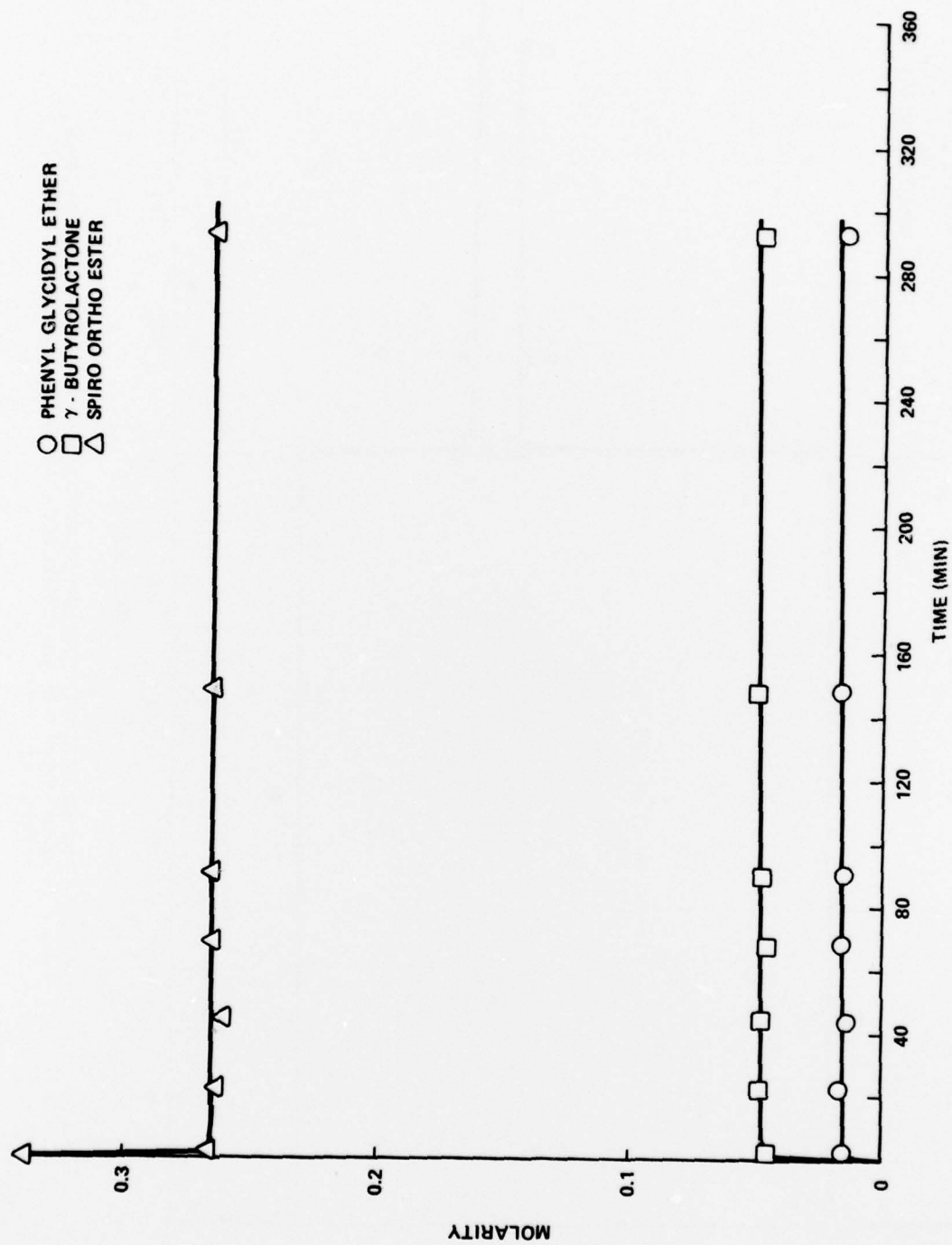


FIGURE 7 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT -30°C AND FIVE MOLE PERCENT CATALYST

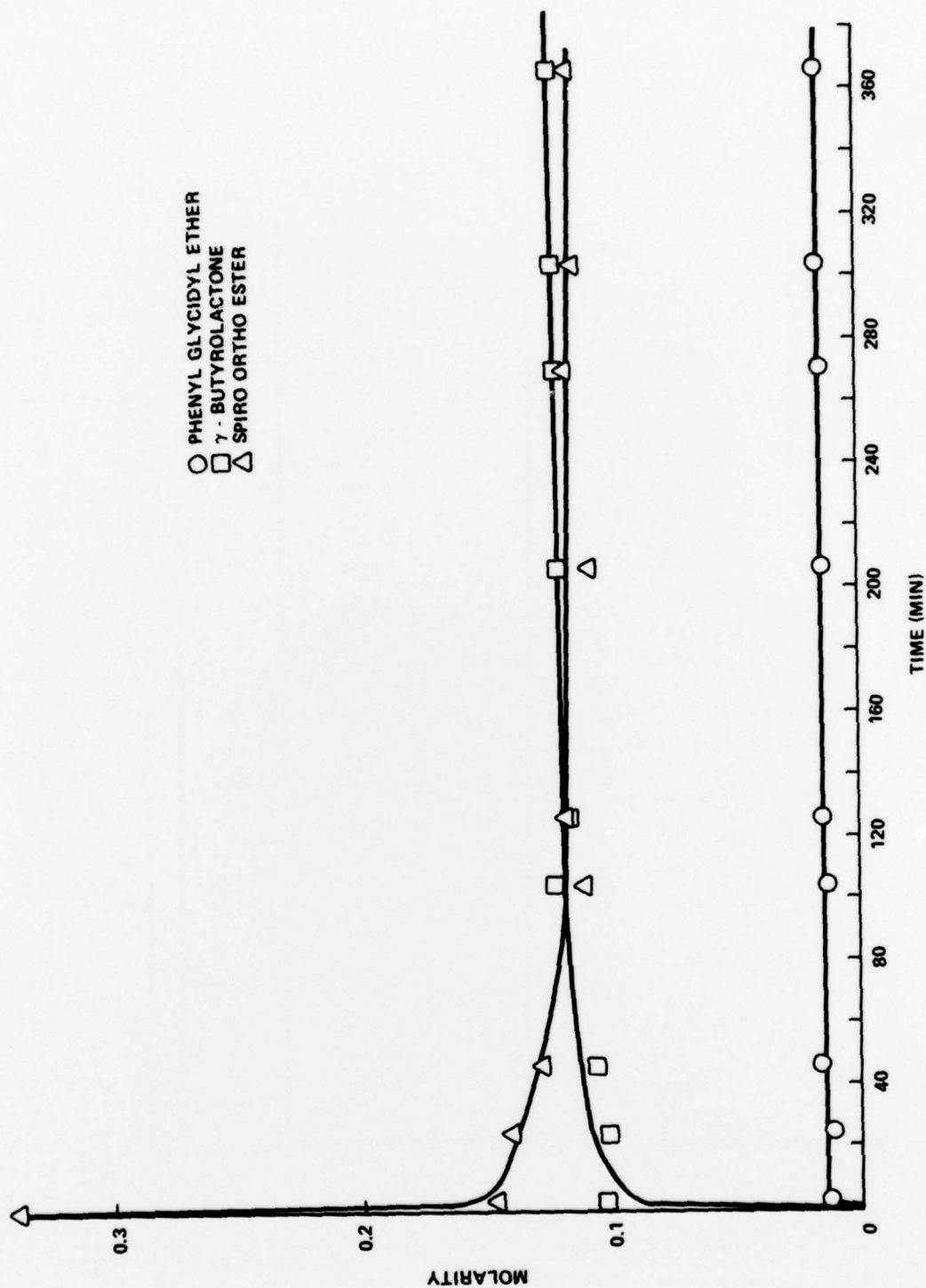


FIGURE 8 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT -30°C AND TEN MOLE PERCENT CATALYST

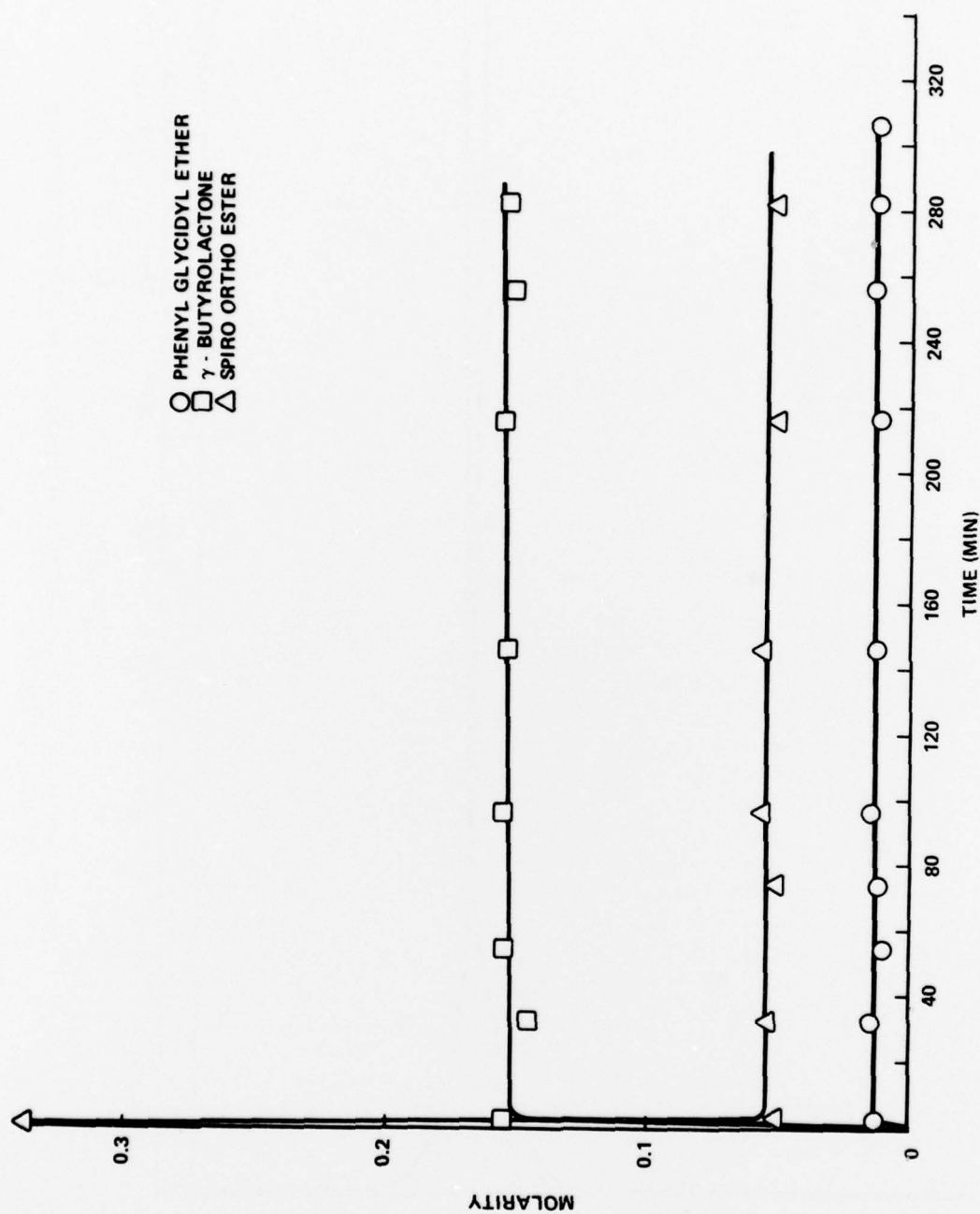


FIGURE 9 POLYMERIZATION OF THE SPIRO ORTHO ESTER I AT -30°C AND TWENTY MOLE PERCENT CATALYST

CONCLUSIONS

The data obtained at the various temperatures and catalyst levels shows that lower temperatures are of no benefit in controlling the side reactions occurring during the polymerization of spiro ortho esters. The concentration of compounds I, II, and III at a particular catalyst level correspond to each other, within experimental error, in the temperature range of -30°C to room temperature.

The quasi-equilibrium concentrations of the spiro ortho ester I and γ -butyrolactone, III, depend on the initial amount of catalyst used. On the other hand, the concentration level of phenyl glycidyl ether, II, is essentially independent of catalyst level. The phenyl glycidyl ether formed upon dissociation of I quickly homo- and copolymerizes until a certain minimum concentration level is reached. This same observation has been noted by Krejear and Lunak.²

2. Krejear, E., and Lunak, S., J. of Polym. Sci., Part C, 16, 643 (1967).

RECOMMENDATIONS

A continued investigation of spiro ortho esters as non-shrinking monomers is not recommended because of competing side reactions during polymerization which lead to polymers of unknown composition and structure.

The use of spiro ortho carbonates as a class of non-shrinking monomers should be investigated. The structure of these materials precludes their breaking down to the compounds from which they are prepared. Some preliminary work has indicated that this class of materials is capable of copolymerization with more conventional acrylic-terminated monomers. The degree of expansion and/or shrinkage, along with a convenient procedure to measure volume change, must be determined. Then, the basic properties of the materials developed can be evaluated.

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